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EUROPEAN ATOMIC ENERGY COMMUNITY – EURATOM

1, 2, 4 - TRIPHENYLBENZENE
SYNTHESIS, PURIFICATION AND PHYSICAL BEHAVIOUR

by

G. BARBERO and F. GEISS

1962

JOINT NUCLEAR RESEARCH CENTER

ISPRA ESTABLISHMENT - ITALY

Chemistry Department

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Summary

1, 2, 4 - triphenylbenzene is one of the products of the radiolysis and pyrolysis of terphenyls which are used as reactor coolants. Overberger has already pointed out that the different synthesis products of other authors were not identical. He also said that different crystal structures of the same compound are likely to exist.

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1 — INTRODUCTION

1,2,4-triphenylbenzene is supposed to be one of the products in radiolysis mixtures of polyphenyls. It is not commercially available. That is the reason why we started its synthesis. Searching in literature we found that nine different ways of synthesis for this compound are described:

1) Trimerisation of phenylacetylene in the presence of bis(triphenylphosphino)nickel-dicarbonyl (2) — m.p. 109°

2) Treatment of 2,3,5-triphenyl-benzoic-acid with copper chromite (4) — m.p. 99,5-100°

3) Reaction between 3,4-diphenyl-4-hydroxy-2-cyclopentenone and phenylacetylene (4) — fractions of 96-99° and 119-120°

4) Dimerisation of 1,3-diphenyl-1,3-butadiene to 4-trans-styryl-1,3,4-triphenylhexene followed by treatment with palladium/charcoal (5) — m.p. 96-99,5°

5) Treatment of the mixed anhydride of acetylene-dicarbonic acid and acetic acid (AcOC ≡ COAc) in the presence of bis-(tetracarbonyl-cobalto)-mercury, besides millitates, hexaethylbenzenes and 1,3,5-triphenylbenzene (3) — m.p. 120-121°

6) Reaction between 4-lithium-m-terphenyl and cyclohexanone succeeded by aromatization (6) — m.p. 96-97°

7) Reaction of 3,4-diphenylthiophene-1,1-dioxide with phenylacetylene (1) — m.p. 100°

8) Reaction of 2,5-diphenylthiophene-1,1-dioxide with phenylacetylene (1) — m.p. 100°

9) Reaction of α acetoxystyrene with 3,4-diphenylthiophene-1,1-dioxide (1) — m.p. 100°

The melting points reported in these publications are evidently crowded around three temperatures:

100°, 109° and 120° C.

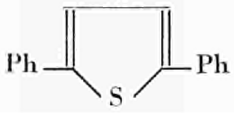
Overberger (1) established that the compound synthetized by *J.D. Rose* (2) (synthesis number 1 of the above list) by means of trimerisation of phenylacetylene was erroneously assumed to be 1,2,4-triphenylbenzene. Furthermore *Overberger* synthetized an identical product by three structurally independent ways, melting at 100°. This one could be converted into a form melting at 119-120° by seeding a melt with a sample obtained by *Halleux* (3) (synthesis 5 of the above list).

2 — SYNTHESIS

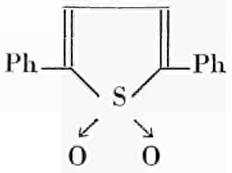
On the basis of this knowledge we repeated one synthesis described by *Overberger* (number 8 of the list). The reaction steps are as follows:

Ph-CO-CH=CH-CO-Ph $\xrightarrow[EtOH]{SnCl_2/HCl}$ Ph-CO-CH_2-CH_2-CO-Ph $\xrightarrow{P_2S_3}$

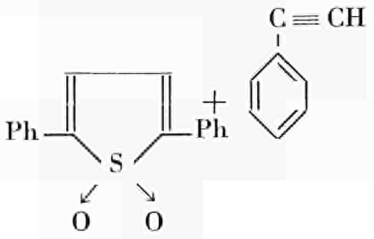
1,2-dibenzoyl-acetylene — 1,2-dibenzoyl-ethane



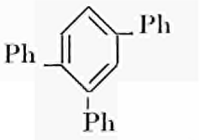
$\xrightarrow[CH_3COOH]{H_2O_2}$



2,5-Diphenylthiophene — 2,5-Diphenylthiophene-1,1-dioxide



$\xrightarrow[-\ SO_2]{135°}$



2,5-Diphenylthiophen + Phenylacetylene -1,1-dioxyde — 1,2,4-Triphenylbenzene m.p. 119°

3 — PURIFICATION

That last step of the above synthesis was a chromatographic purification of the reaction products. The description of process was rather vague. We divided the eluate (with petrolether-benzene 1:4) into eight fractions in an arbitrary manner. In order to find out in which of the fractions the desired compound was present, we carried out a comparative *thin layer chromatogram* of the single fractions and of a sample of the Progil company (Lyon, France) trapped by fractionation of a terphenyl residue.

Discussion of the Thin layer chromatogram (Fig. 1)

The first seven rows from left to right are the fractions 2 to 8 of the eluate, the next row represents the total mixture before separation and the last one on the right is the Progil sample. There are some six or seven reaction products visualized, the most important of which is present in all fractions and evidently identical with the Progil sample. All the spots which are on the same level as the Progil sample have the same brownish colour after treatment with the spray reagent Cerium-(IV)-sulphate/conc. nitric acid.

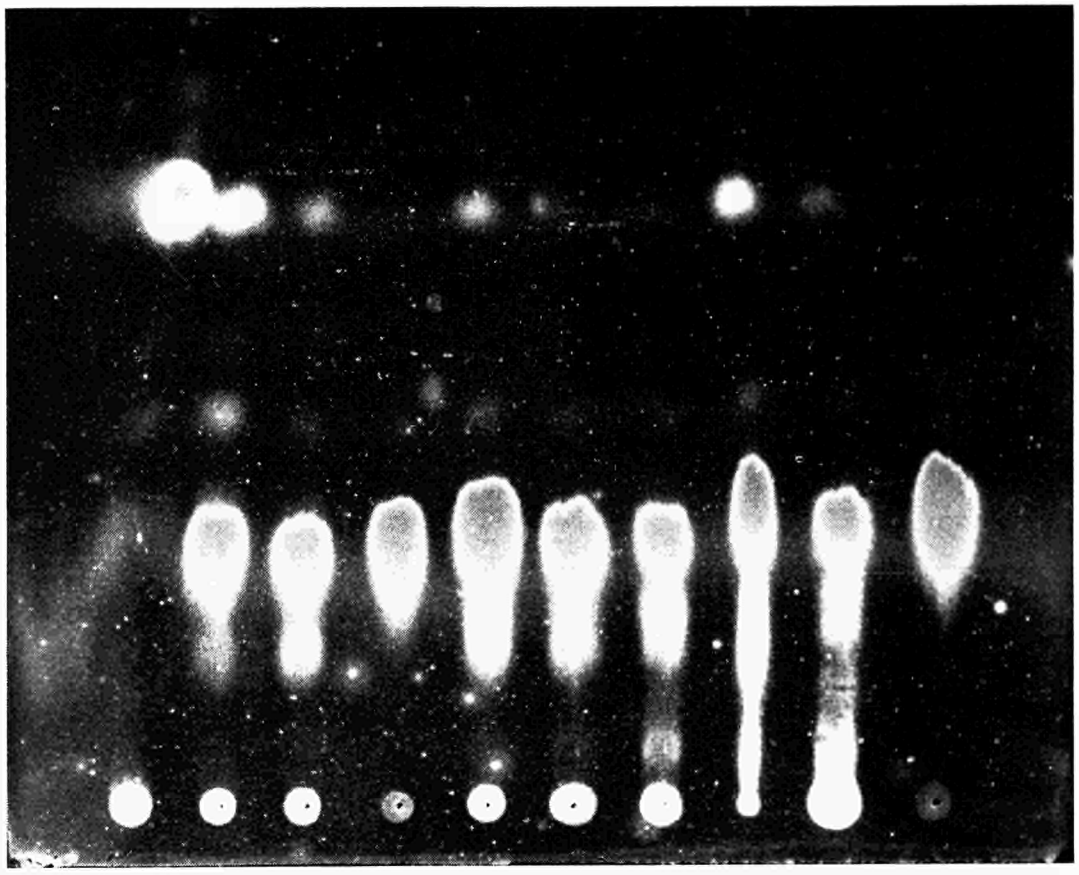


Figure 1. — Thin layer chromatogram of the column eluates. Separation of the reaction products of the last step.

from left to right	Start	1	fraction 2 of elution	1 µg
		2	3	1 µg
		3	4	1 µg
		4	5	1 µg
		5	6	1 µg
		6	7	not determined
		7		not determined
		8	mixture before separation	not determined
		9	residue of petrolether extr.	not determined
		10	sample of Progil	1 µg

Plate coating : Aluminiumoxyd zur Dünnschichtchromatographie, Merck, eluent: n-heptane. Colours in long wave UV-light (after treating with 0,3 % Ce_2SO_4/HNO_3 conc. spray reagent) : 1, 2, 4 - triphenylbenzene : brown, phenylacetylene : yellow, compound below 1, 2, 4 - triphenylbenzene : red, the lowest spots off the start : bright clear.

The first spot on the left (second fraction) represents exceeding phenylacetylene left from the reaction. Except 1,2,4-triphenylbenzene, the other spots could not be identified yet. In any case the reaction gives a yield of 1,2,4-triphenyl-benzene lower than 10 % instead of 45 % as indicated by *Overberger*.

4 — PHYSICAL DATA

UV: Maximum at 2480 A
Inflection at 2700 A

identical for both of the crystal forms

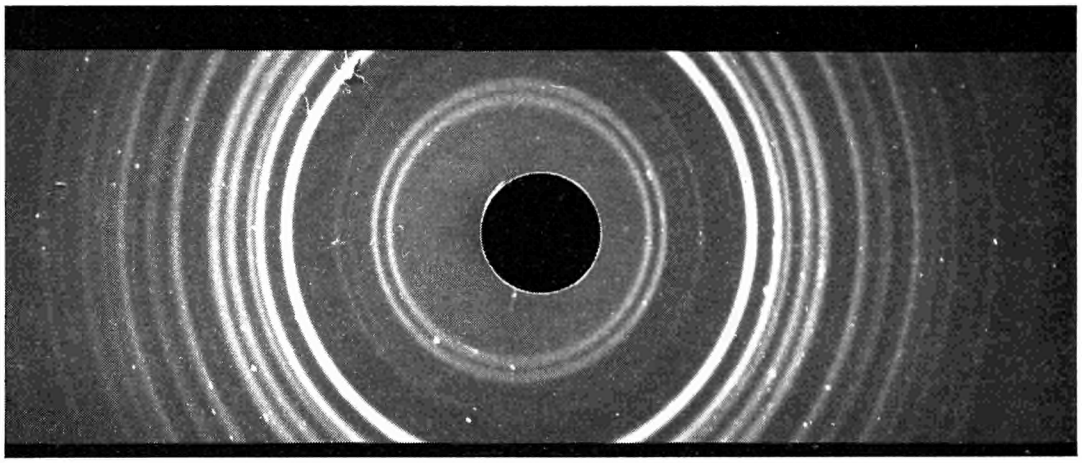
IR: *Overberger* recorded his spectra in carbon tetrachloride solution. This is not worth while being repeated because all specific vibrations are placed in the 820-725 cm^{-1} range where carbon tetrachloride absorbs too strongly. We took the spectra in potassium bromide pellets:

1460, 1440, 1385, 1070, 1025, 1005, 890, 835, 775, 760, 735 cm^{-1}.

The optical characteristics of the synthetical product and the Progil sample are identical.

Comparison of Melting points

	Material	m.p. raw (°C)	colour	m.p. recrystall.	colour
1	fraction 3	91	yellow	—	—
2	fraction 4	99-99,5	yellow	119,5	colourless
3	fraction 5	118-119	yellow	119,5	colourless
4	fraction 6	115-116	yellow	119,5	colourless
5	Progil sample	92-93	yellow	95-95,5	colourless
6	mixed m.p. fr. 4 and Progil sample with intermediate solidification			1st 92-100 2nd 99,5-109 3rd 111,5-116	—



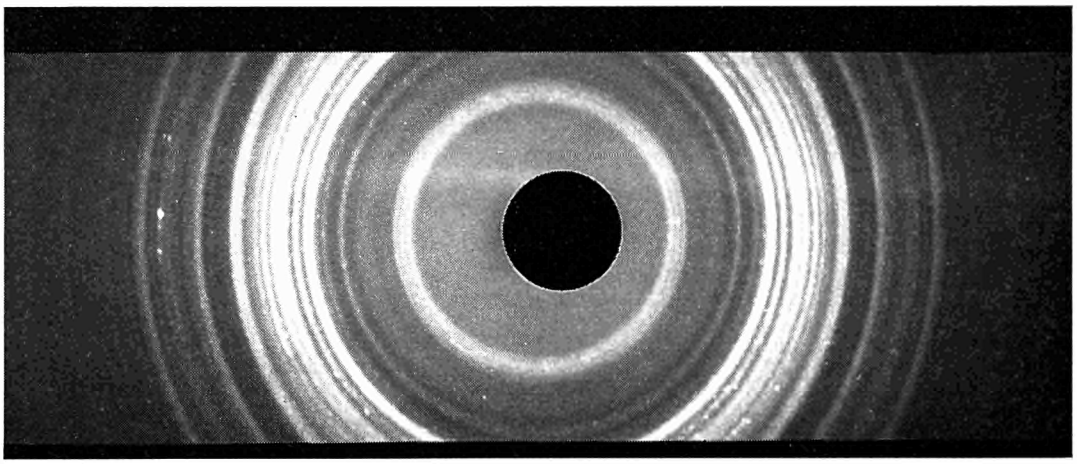


Figure 2. — Debye-Scherrer patterns of the two crystal forms of 1, 2, 4 - triphenyl-benzene.
The top figure shows the form melting at 119,5° C, the figure below the form melting at 95-95,5° (containing a small amount of impurity).

5 — CONCLUSIONS

Thus, the following conclusions can be drawn:

1) The Progil sample is chemically identical with the 1,2,4-triphenylbenzene synthetized by us.

2) In spite of the same way of synthesis our compound* melts at 119,5° in contrast to Overberger's which melts at 99°. They represent the two crystal structures of the compound.

3) From the terphenyl distillation residue the lower melting form was trapped.

4) The lower melting form can be converted to the higher melting form by repeated mixed melting.

5) The Progil sample seems to be accompanied by a small amount of impurities with depressed both melting point and mixed melting point for some 3°. Thus, the presence of an impurity is apparent, but could not yet be visualized.

6) There is no noticeable difference between the IR-absorption of the two crystalline forms in KBr-pellets, however, the Debye-Scherrer patterns (fig. 2) definitely confirm the existence of two different forms of crystals.

This investigation has been carried out in the Euratom Joint Research Centre of Ispra (Italy) within the framework of the "Orgel" reactor programme.

* The synthesis was repeated twice.

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